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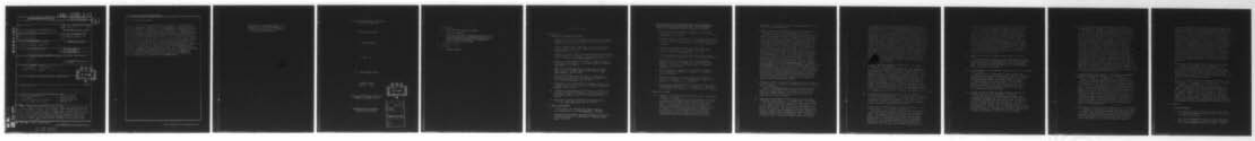

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8. quantum beats

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Radiationless transitions concern the way energy is stored, exchanged and utilized in chemical systems. It is therefore a more important area of study than the radiative transitions which accompany them. The main thrust of the research was to modernize the theory of radiationless transitions in polyatomic molecules, and to utilize the intuition gained for suggesting interesting picosecond experiments dealing with energy exchange and other types of radiationless processes. The theory, which is based upon field and scattering

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theories, is closely connected with the density matrix and the information theoretic approaches. However, it has the advantage of being better able to utilize semiempirical information, such as absorption and scattering spectra. The main results of the work can be listed as follows: (1) unification of the radiation-matter time-dependent interaction theories of Raman scattering, Rayleigh scattering, absorption-fluorescence spectroscopy, with or without the presence of radiationless transitions; (2) the discovery and development of methods whereby certain complex, vibronically mixed spectra of polyatomic molecules can be "untangled" so that they can be analyzed by ordinary spectroscopic methods; (3) the theoretical investigation of a mechanism for the extremely rapid radiationless loss of energy following absorption of ionizing radiation by a material; (4) initiation of some picosecond spectroscopic experiments using a Nd^{+3}/glass mode-locked laser; (5) a detailed theoretical analysis suggesting how "quantum beats" and other types of nonexponential decays could be studied by picosecond spectroscopy; and (6) some suggestions concerning methods by which photochemical yields can be changed through subtle variations of the light source by an experimenter.

THE FINDINGS IN THIS REPORT ARE NOT TO BE CONSTRUED AS AN OFFICIAL DEPARTMENT OF THE ARMY POSITION, UNLESS SO DESIGNATED BY OTHER AUTHORIZED DOCUMENTS.

PICOSECOND RADIATIONLESS TRANSITIONS IN POLYATOMIC MOLECULES

FINAL TECHNICAL REPORT

G. WILSE ROBINSON

19 MAY, 1977

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Index

Body of Final Report

I. PUBLICATIONS

A. Papers published under the contract.

1. "Molecular Electronic Radiationless Transitions," from Excited States, E. C. Lim, Ed., G. Wilse Robinson, Academic Press, New York, 1974, Vol. I, pp. 1-34.

2. Theory of Radiationless Transitions in Polyatomic Molecules. The Intermediate Case, G. W. Robinson and C. A. Langhoff, Chemical Phys., 5, 1 (1974).

3. Dominance of Methyl Groups in Picosecond Vibrational Relaxation in Hydrocarbons, P. R. Monson, S. Patumtevapibal, K. J. Kaufman, and G. W. Robinson, Chem. Phys. Letters, 28, 312 (1974).

4. Time Decay and Untangling of Vibronically Tangled Resonances: Naphthalene Second Singlet, C. A. Langhoff and G. W. Robinson, Chem. Phys., 5, 34 (1974).

5. Theory of Time-Resolved Resonance Scattering, Jacqueline O. Berg, Charles A. Langhoff, and G. Wilse Robinson, Chem. Phys. Letters., 29, 305 (1974).

6. The Level Shift Operator and Its Effect on Line Shapes in Vibronically Perturbed Spectra, Charles A. Langhoff and G. Wilse Robinson, Mol. Phys., 29, 613 (1975).

7. An Approach to the Understanding of Radiation Chemistry in the Condensed Phase, J. O. Berg and G. W. Robinson, Chem. Phys. Letters, 34, 211 (1975).

8. Lineshape-Lifetime Relationship and Emission and Scattering of Light by Polyatomic Molecules, G. W. Robinson and J. O. Berg, Can. J. Phys., 53, 2068 (1975) Herzberg Festschrift Edition.

9. Extraction of Vibronic Information from Tangled Spectra, J. O. Berg, Chem. Phys. Lett., 41, 547 (1976).

B. Papers in preparation.

1. A Unified Theory of Time-Dependent Light Scattering, G. W. Robinson and J. O. Berg, Chem. Phys., submitted.

2. Resonant and Near-Resonant Rayleigh and Raman Scattering for a Diatomic Molecule, J. O. Berg and G. W. Robinson, Chem. Phys., submitted.

C. Papers published and in preparation joint with the Australian Research Grants Committee and which will form the foundation papers of a continuing ARO Grant at Texas Tech University.

1. Direct Observation of Rotational Diffusion by Picosecond Spectroscopy, G. R. Fleming, J. M. Morris, and G. W. Robinson, Chem. Phys., 17 91 (1976).

2. Picosecond Spectroscopic Studies of Spontaneous and Stimulated Emission in Organic Dye Molecules, G. R. Fleming, A.E.W. Knight, J. M. Morris, R. J. Robbins, and G. W. Robinson, Chem. Phys., accepted.

3. Picosecond Fluorescence Studies of Xanthene Dyes, G. R. Fleming, A.E.W. Knight, J. M. Morris, R.J.S. Morrison, and G. W. Robinson, J. Am. Chem. Soc., accepted.

4. Picosecond Fluorescence Spectroscopy Using a Streak Camera, G. R. Fleming, J. M. Morris, and G. W. Robinson, in preparation.

5. Properties of Single Picosecond Pulses from Neodymium: Phosphate Glass, G. R. Fleming, I. R. Harrowfield, A.E.W. Knight, J. M. Morris, R. J. Robbins, and G. W. Robinson, Opt. Comm., 20, 36 (1977).

6. Exciton Fission and Annihilation in Crystalline Tetracene, G. R. Fleming, D. P. Millar, G. C. Morris, J. M. Morris, and G. W. Robinson.

7. Rotational Diffusion as a Probe for Molecular Conformation and Solvent Attachment, G. R. Fleming, A.E.W. Knight, J. M. Morris, R. J. Robbins, and G. W. Robinson.

8. Spectral and Temporal Bandwidths of the Harmonics of A Mode-Locked Nd^{+3}/phosphate Glass, G. R. Fleming, I. R. Harrowfield, A.E.W. Knight, J. M. Morris, R. J. Robbins, and G. W. Robinson.

II. ABSTRACTS OF PAPERS

A1. "Molecular Electronic Radiationless Transitions," from Excited States, G. W. Robinson.

This is a review article with 103 references of work on quantum mechanical radiationless transitions from the inception of the field in 1927 to 1974. The review not only covers the "pretheoretical period" before the Robinson-Frosch papers in 1960-1962, but also the intermediate period of research in this area which was directly stimulated by the R-F papers, up to the present era, where the field theoretic approach and the close relationship between radiationless processes, absorption spectroscopy, and the

dependence of the prepared state on the experimentalist's light source are strongly emphasized.

A2. Theory of Radiationless Transitions in Polyatomic Molecules. The Intermediate Case, G. W. Robinson and C. A. Langhoff.

A theory of radiationless transitions that spans the intermediate case between the "small molecule" and "big molecule" limits is presented. The theory is applicable to spectra and picosecond time evolution experiments concerning states such as the vibronically perturbed second excited singlet state of naphthalene studied by Wessel. An important philosophy used in the papers is the "unbundling" of the time-dependent and stationary state aspects of this problem. This view has been strongly emphasized by Rhodes and allows each part of the problem to be handled separately without being limited by the approximations of the other. The single-sharp-level-embedded-in-a-continuum model is used, and the stipulation that the sharp level carries all the oscillator strength is retained. However no limiting restrictions are placed on the nature of the continuum nor the interaction matrix elements. Thus the theory encompasses both the statistical limit and the small molecule limit as well as all cases intermediate between these and should therefore be of more interest to the experimentalist. The exact Green function for this problem is obtained, allowing the observed absorption spectrum and time evolution experiments under various excitation conditions to be exactly related in a practical way. Transformation between an observed spectrum and unperturbed zero-order states is possible and should be of use to the spectroscopist when trying to analyze spectra in regions of massive perturbative mixing.

A3. Dominance of Methyl Groups in Picosecond Vibrational Relaxation in Hydrocarbons, P. R. Monson, S. Patumtevapibal, K. J. Kaufmann, and G. W. Robinson.

Picosecond relaxation times of C—H stretching vibrations in a series of liquid hydrocarbons have been measured using the Raman scattering technique. The results indicate that the vibrational energy loss takes place primarily through the methyl groups in these molecules.

A4. Time Decay and Untangling of Vibronically Tangled Resonances: Naphthalene Second Singlet, C. A. Langhoff and G. W. Robinson.

The Green function method is used to explain quantitatively the very complex spectrum of naphthalene in the region of the second excited singlet state ($^1B_{2u}$) studied experimentally by McClure and by Wessel. The $^1B_{2u}$ state strongly interacts with a mass of vibronic levels belonging to the lower singlet ($^1B_{3u}$) causing a complete lack of correspondence between the zero-order energy levels and the observed spectrum. In the spirit of Wessel's ideas, a zero-order density can be derived from

the observed spectrum, allowing the spectroscopic analysis to be continued from the weakly perturbed region into the strongly perturbed "resonance". The vibronic assignments can be made to within a 2-3 cm^{-1} accuracy. This spectral region also presents a good example of the "intermediate case" in radiationless transition theory, and under suitable excitation would give rise to complicated, nonexponential fluorescence decay, with low overall fluorescence yield. A dispersion relationship, derived earlier, allows the real and imaginary parts of the Green function to be obtained from the absorption spectrum. When these terms are used in the time evolution equations under various light source excitations, fluorescence decay curves can be calculated. The decay curves exhibit well-defined picosecond or subpicosecond "beats", but commencing at intensities at least two orders of magnitude below that of the initial (t=0) intensity. Using present picosecond technology, the beats would be difficult to detect. The naphthalene case gives but one example of a molecule having "vibronically tangled resonances"; many other large polyatomic molecules as well as smaller molecules like NO_2, SO_2, and CS_2 show similar complications.

A5. Theory of Time-Resolved Resonance Scattering, J. O. Berg, C. A. Langhoff, and G. W. Robinson.

A theory is presented that describes the time dependence of scattering off an atomic or molecular "resonance" using tunable dye laser pulses. The main conclusion is that there is no exponentially decaying component which depends upon the frequency difference between the exciting pulse and the resonance. In the limit of extremely narrowbanded excitation, all time resolution is lost, and the usual resonance scattering intensity formulas are obtained. In the opposite limit, where the excitation is broad-banded, formulas describing fluorescence decay emerge. The time evolution for the case of more than a single resonance can be obtained numerically, but an analytical expression is possible for the steady state scattering amplitude from two resonances, from which exact resonance Raman formulas can be found.

A6. The Level Shift Operator and its Effects On Line Shapes In Vibronically Perturbed Spectra, C. A. Langhoff and G. W. Robinson.

This paper discusses the role of the level shift operator in vibronically mixed molecular resonances. The effect of this operator on the shapes of resonances is particularly important when the resonances contain resolved structure.

A7. An Approach To The Understanding of Radiation Chemistry in the Condensed Phase, J. O. Berg and G. W. Robinson.

This paper describes a purely electronic mechanism by which $\simeq$ 20 eV excitations in condensed phases relax to lower energy states. The mechanism utilizes an "energy fission" process whereby an ionic or excitonic state splits into two lower energy states, at least one being localized. The mechanism explains not only the known rapidity of such processes but also suggests an explanation for the proportionation of the chemistry between ionic and electronically excited states.

A8. Line Shape - Lifetime Relationship and Emission and Scattering of Light by Polyatomic Molecules, G. W. Robinson and J. O. Berg.

A unified theory of ordinary Rayleigh scattering, Raman scattering, and the absorption and reemission of light is presented and discussed from an experimental spectroscopist's point of view. Application to polyatomic molecules presents unique problems which are discussed. The theory should be able to account for experimental results off, near, and on resonance, using weak exciting light sources of various band shapes. The evolution of the Frank-Condon envelope on nearing the resonance region is described, and time dependent aspects of the interaction are treated in a general way. The theory in its present form cannot be used when the light source is so intense that population inversion, multiphoton effects, and stimulated processes take place.

A9. Extraction of Vibronic Information From Tangled Spectra, J. O. Berg.

A new method of calculating the zero-order density function directly from the absorption spectrum has been found and applied to the origin region of naphthalene's second excited singlet state. Results are in good agreement with the tiral-and-error method of Langhoff and Robinson.

B1. A Unified Theory of Time-Dependent Light Scattering, G. W. Robinson and J. O. Berg.

A unified theory is presented for time-dependent light scattering of an uncertainty-limited pulse from far off-resonance into the resonance region. The theory reduces to the conventional Kramers-Heisenberg second-order perturbation result if a monochromatic light source is used. The two photon-states' contribution to the scattering cross section has the same time dependence as the light source, while the zero-photon state has the time-dependence previously calculated for near-resonance light scattering.

B2. Resonant and Near-Resonant Rayleigh and Raman Scattering for A Diatomic Molecule, J. O. Berg and G. W. Robinson.

Using the results of the preceeding paper in the time-independent (narrow exciting line) limit, excitation profiles for Rayleigh and Raman cross sections have been calculted for an actual diatomic molecule from over 8000 cm^{-1} off resonance into the resonance region. Three interference effects, a "vibrational level interference", an "on-resonance Franck-Condon interference", and an "off-resonance interference" are discussed. The usual formula for scattering cross section is shown to lead to errors off-resonance if the basis set is truncated.

C1. Direct Observation of Rotational Diffusion by Picosecond Spectroscopy, G. R. Fleming, J. M. Morris, and G. W. Robinson.

Time dependent fluorescence depolarization measurements have for the first time been extended to the picosecond regime by using streak camera optical multichannel analyzer detection. Fluorescein derivative dyes (M.W. 500-1000) rotate in polar solvents as if their volume is at least double that of the free molecule because of solvent attachment, an effect noted by Einstein and elaborated upon by Marinesco and Perrin many years ago. This effect is apparently the major cause of the breakdown of the literal Einstein hydrodynamic model for rotation of these relatively small molecules in solution. The solvent attachment also very likely reduces the effect of molecular shape on rotational depolarization, causing these molecules to behave more like spheres than their molecular structure would imply. Both the fluorescence decay curve and the rotational correlation function derived from the experimental data, within the limits of experimental error, decay as pure exponentials. In addition, unlike most fluorescence probe experiments on nanosecond time scales applied to the study of macromolecular structure, the theoretical value of 0.4 for the polarization anisotropy at zero time is observed. Comparison of these types of results on picosecond time scales could have implications on the study of flexions and rotations of the substructure of large molecules having biological importance.

C2. Picosecond Spectroscopic Studies of Spontaneous and Stimulated Emission in Organic Dye Molecules, G. R. Fleming, A. E. W. Knight, J. M. Morris, R. J. Robbins, and G. W. Robinson.

Stimulated emission from organic dyes provides us with the potential for producing tunable, short pulsed lasers. Stimulated emission can also interfere in the measurement of excited state lifetimes of dyes when excited by intense picosecond pulses. Time-resolved measurements of the emission from several organic dyes as a function of excitation intensity have been carried out in order to determine the conditions for obtaining efficient dye lasers and correct excited state lifetimes. A long build-up time for the stimulated emission ($\sim$ 60 psec for a 6-8 psec exciting pulse) has been observed and confirmed by a theoretical model. Calculations using this model show that, even in the presence of very weak stimulated emission, the emission intensity does not decay in the same manner as the density of excited molecules.

C3. Picosecond Fluorescence Studies of Xanthene Dyes, G. R. Fleming, A.E.W. Knight, J. M. Morris, R.J.S. Morrison, and G. W. Robinson.

Subnanosecond lifetime measurements using picosecond pulses from a mode locked Nd^{+3}/glass laser together with conventional absorption and fluorescence yield methods have been used to study the photophysics of fluorescein and three of its halogenated derivatives (eosin, erythrosin and rose bengal) in

aqueous and simple alcoholic solvents. For each of the dye molecules absorption and fluorescence maxima move towards higher energy ("blue shift") as the solvent changes from iPrOH to H_2O. Fluorescence lifetimes and quantum yields are found to decrease markedly with this solvent change, and also with increased halogenation ("heavy atom effect") of the fluorescein parent. Published triplet yield data confirm that the variations observed in the nonradiative part of the decay rate can be attributed almost wholly to variations in the rate of S_1-T_1 intersystem crossing. A simple and reasonable explanation of the observed effects can be found if for these particular solvent-solute combinations, stabilization energies lie in the order $\Delta E(T_1) < \Delta E(S_1) < \Delta E(S_0)$. This idea is consistent with both the increased S_1-S_0 spectral "blue shifts" and the enhanced intersystem crossing rate, arising from a smaller S_1- T_1 energy gap, when these dye molecules are placed in a more aqueous solvent environment. The studies are relevant to the use of these dyes as fluorescent probes in biologically important molecules.

C4. Picosecond Fluorescence Spectroscopy Using a Streak Camera, G. R. Fleming, J. M. Morris, and G. W. Robinson.

This paper describes the first streak-camera-optical-multichannel-analyzer detection system for picosecond pulse spectroscopy. A similar system has been set up at Texas Tech University and is the basis for research under ARO grant DAAG29-76-G-0289 during the latter half of 1976 and a continuing grant DAAG-29-77-G-0028 now in progress.

C5. Properties of Single Picosecond Pulses from Neodymium: Phosphate Glass, G. R. Fleming, I. R. Harrowfield, A.E.W. Knight, J. M. Morris, R. J. Robbins, and G. W. Robinson.

Streak camera detection has been used to determine the temporal characteristics of pulses from Nd:phosphate glass used as a mode-locked laser oscillator and as an amplifier. The frequency doubled pulses are not transform limited ($\Delta\nu$ = 46 cm^{-1}, $\Delta\tau$ = 6ps). The fourth harmonic has a spectral bandwidth of 11 cm^{-1} and is tunable across the full bandwidth of the second harmonic. Temperature tuning characteristics and efficiencies for harmonic generation are described A comparison is made with the properties of Nd:silicate glass.

III. PERSONNEL

A. Graduate students.

1. Mr. Charles A. Langhoff received his PhD in June, 1974. He is now an assistant professor of chemistry at Illinois Institute of Technology.

2. Ms. Sa-on Patumtevapibal received her PhD in June, 1975. She was partly supported by a Thai government fellowship and is back in Bangkok teaching in a woman's college.

3. Ms. Jacqueline O. Berg finished the work for her PhD in September, 1976. She will officially receive this degree from Caltech in June, 1977, and is now working as a post-doctoral fellow with Professor M. A. El-Sayed at U.C.L.A.